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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>B32B 5/28, 27/32</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/12302</b> <b>(43) International Publication Date:</b> 9 March 2000 (09.03.00)
<b>(21) International Application Number:</b> PCT/US99/19788 <b>(22) International Filing Date:</b> 27 August 1999 (27.08.99)  <b>(30) Priority Data:</b> 09/145,949 2 September 1998 (02.09.98) US  <b>(71) Applicant:</b> MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US).  <b>(72) Inventors:</b> AGENT, Rhonda, Rogers; 241 Townsend Street, Rochester, NY 14621 (US). PIP, Hans, Joachim; 167, rue de Sesselich, B-6700 Arlon (BE).  <b>(74) Agent:</b> ALEXANDER, David, J.; ExxonMobile Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US).		<b>(81) Designated States:</b> AU, BR, CA, CN, ID, JP, KR, SG, VN, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> BIORIENTED POLYETHYLENE FILM WITH A HIGH WATER VAPOR TRANSMISSION RATE  <b>(57) Abstract</b> <p>Polyethylene films having desired water vapor transmission rates (WVTR) and methods of producing the same are provided. The methods include adherently superimposing at least one layer of a WVTR-controlling material to a base layer including a polyethylene and a cavitating agent, and subsequently biaxially orienting the composite polyethylene sheet to yield a film having the desired WVTR. The base layer has a porous microstructure and a WVTR substantially higher than the desired WVTR.</p>		

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**BIORIENTED POLYETHYLENE FILM  
WITH A HIGH WATER VAPOR TRANSMISSION RATE**

The present invention relates to polymer films and methods for preparing polymer films.  
5 Specifically, the present invention relates to bioriented polyethylene films having high water vapor transmission rates (WVTR) and methods of preparing the same.

Generally, in the preparation of a film from granular or pelleted polymer resin, the polymer is first extruded to provide a stream of polymer melt, and then the extruded polymer is subjected to the film-making process. Film-making typically involves a number of discrete  
10 procedural stages, including melt film formation, quenching, and windup. For a general description of these and other processes associated with film-making, see KR Osborn and WA Jenkins, *Plastic Films: Technology and Packaging Applications*, Technomic Publishing Co., Inc., Lancaster, Pennsylvania (1992).

An optional part of the film-making process is a procedure known as "orientation." The  
15 "orientation" of a polymer is a reference to its molecular organization, i.e., the orientation of molecules relative to each other. Similarly, the process of "orientation" is the process by which directionality (orientation) is imposed upon the polymeric arrangements in the film. The process of orientation is employed to impart desirable properties to films, including making cast films tougher (higher tensile properties). Depending on whether the film is made by  
20 casting as a flat film or by blowing as a tubular film, the orientation process requires substantially different procedures. This is related to the different physical characteristics possessed by films made by the two conventional film-making processes: casting and blowing. Generally, blown films tend to have greater stiffness, toughness and barrier properties. By contrast, cast films usually have the advantages of greater film clarity and uniformity of  
25 thickness and flatness, generally permitting use of a wider range of polymers and producing a higher quality film.

Orientation is accomplished by heating a polymer to a temperature at or above its glass-transition temperature ( $T_g$ ) but below its crystalline melting point ( $T_m$ ), and then stretching the film quickly. On cooling, the molecular alignment imposed by the stretching competes  
30 favorably with crystallization and the drawn polymer molecules condense into a crystalline network with crystalline domains (crystallites) aligned in the direction of the drawing force.

As a general rule, the degree of orientation is proportional to the amount of stretch, and inversely related to the temperature at which the stretching is performed. For example, if a base material is stretched to twice its original length (2:1) at a higher temperature, the orientation in the resulting film will tend to be less than that in another film stretched 2:1 but at a lower temperature. Moreover, higher orientation also generally correlates with a higher modulus, i.e., measurably higher stiffness and strength. Further, as a general rule, higher orientation correlates with lower WVTR values for films.

Previously, high WVTR values have been difficult to achieve with polyolefin films. Typically, film production methods aim to lower WVTR values for polyolefin films. As such, polyolefin films inherently have low WVTR values compared to traditional wrapping materials such as cellulose films or paper.

Accordingly, it is one of the purposes of this invention, among others, to produce bioriented polyethylene films having high WVTR values, by providing an economical and relatively uncomplicated method of making polyethylene films that imparts superior characteristics to the films, without requirement for chemical additives such as cross-linking agents, and without requirement for supplemental processing steps such as irradiation of the film.

It has now been discovered that these and other purposes can be achieved by the present invention, which provides for bioriented polyethylene films having high WVTR values and methods of producing the same.

Various structured polyethylene films having high WVTR can be produced by the methods of the present invention. One embodiment of the present invention provides for a film having a base layer and at least one layer of a WVTR controlling material whereby the polyethylene film has a desired WVTR and the base layer has a porous microstructure and WVTR substantially higher than the desired WVTR for the polyethylene film. The base layer includes polyethylene and a cavitating agent, and preferably, the polyethylene is a medium density polyethylene (MDPE) or a high density polyethylene (HDPE). The base layer also has a first side and a second side. Further, the base layer preferably has a thickness of from 0.5 mil to 2.0 mil (1 mil = 0.001 inch = 100 gauge). It should be noted that any thickness value provided herein does not account for additional thickness resulting from cavitation.

The WVTR-controlling layer of the polyethylene film is coextensive with one of the sides of the base layer and includes a WVTR-controlling material, either a MDPE or a HDPE, which should not have a density greater than that of the polyethylene in the base layer. Further, it is preferable that the WVTR-controlling layer have a thickness of from 0.03 mil (3  
5 gauge) to 0.15 mil (15 gauge).

A preferred embodiment of the present invention provides for a film having the desired WVTR and having a tie layer interposed between a base layer and a WVTR-controlling layer wherein the tie layer is coextensive with each of the base layer and the WVTR-controlling layer. The base layer, which includes polyethylene and a cavitating agent, has a first side and a  
10 second side. Further, the base layer has a porous microstructure and a WVTR substantially higher than the desired WVTR for the polyethylene film. Preferably, the WVTR-controlling layer includes a WVTR-controlling material of either MDPE or HDPE. Alternatively, the WVTR-controlling material can be either an ethylene-propylene copolymer or an ethylene-propylene-butylene terpolymer wherein the tie layer would be either a MDPE or a blend of  
15 HDPE and low density polyethylene (LDPE).

Another preferred embodiment of the present invention provides for a film having the desired WVTR wherein the film has first and second layers of a WVTR-controlling material coextensive with the first and second sides of the base layer. The base layer, which includes polyethylene and a cavitating agent, has a porous microstructure and a WVTR substantially  
20 higher than the desired WVTR for the polyethylene film. The first and second WVTR-controlling layers should each include a WVTR-controlling material of preferably either a MDPE or a HDPE.

Another preferred embodiment of the present invention provides for a film wherein a first tie layer is interposed between a base layer and a first WVTR-controlling layer and a second  
25 tie layer is interposed between the base layer and a second WVTR-controlling layer. The first tie layer is coextensive with each of the base layer and first WVTR-controlling layer and the second tie layer is coextensive with each of the base layer and the second WVTR-controlling layer.

It should be noted that polyethylene films according to the present invention are not  
30 limited to the foregoing structures and can include several layers as a plurality of WVTR-controlling layers or tie layers can be provided to obtain a film having the desired WVTR.

The methods of the present invention provide for adherently superimposing at least one layer of a WVTR-controlling material coextensively to a first side of a base layer having first and second sides and then biaxially orienting the composite polyethylene sheet to obtain a film having a desired WVTR. The base layer of the composite polyethylene sheet includes  
5 polyethylene and a cavitating agent. The composite polyethylene sheet is biaxially oriented whereby there is provided a bioriented polyethylene film having the desired WVTR and whereby the base layer has a porous microstructure and a WVTR substantially higher than the desired WVTR.

Preferably, the polyethylene of the base layer is a MDPE or a HDPE. Further, it is  
10 preferable that the amount of polyethylene provided in the base layer prior to producing a film be an amount sufficient to yield a base layer in the film having a thickness of from 0.5 mil to 2.0 mil. It should be noted that any thickness value provided herein does not account for additional thickness resulting from cavitation. In addition, it is preferable that the WVTR-controlling material is a MDPE or a HDPE, however, the WVTR-controlling material  
15 should not have a density greater than that of the polyethylene in the base layer. Further, it is preferable that the WVTR-controlling material is provided in an amount sufficient to yield a WVTR-controlling layer in the film having a thickness of from 0.03 mil to 0.15 mil.

A preferred method of the present invention provides for producing a film having a three layer structure. In particular, a first layer of a WVTR-controlling material is adherently  
20 superimposed to a first side of a base layer and a second layer of a WVTR-controlling material is adherently superimposed to the second side of the base layer. The composite polyethylene sheet is then biaxially oriented.

Another preferred method of the present invention provides for producing a film having a five layer structure. In particular, a base layer having first and second sides is provided and is  
25 interposed between two tie layers wherein the first tie layer is interposed between the first side of the base layer and a first WVTR-controlling layer, and wherein the second tie layer is interposed between the second side of the base layer and a second WVTR-controlling layer. The tie layers are each adherently superimposed to the base layer and are each coextensive with the base layer. The WVTR-controlling layers are each adherently superimposed to the tie  
30 layers and are each coextensive with their adjacent tie layer. The composite polyethylene

sheet is then biaxially oriented. The tie layers of this structure include MDPE or HDPE and can also include a cavitating agent to regulate the WVTR.

Another method of the present invention provides for producing a film by adherently superimposing at least one tie layer to a base layer wherein the tie layer is coextensive with the  
5 base layer, and further, adherently superimposing a WVTR-controlling layer to the tie layer wherein the WVTR-controlling layer is coextensive with the tie layer. The WVTR-controlling layer comprises a WVTR-controlling material of preferably HDPE or MDPE. The tie layer includes MDPE or HDPE and can also include a cavitating agent to regulate the WVTR. However, an alternative method includes provision for a WVTR-controlling layer including a  
10 WVTR-controlling material of either an ethylene-propylene copolymer or an ethylene-propylene-butylene terpolymer wherein the tie layer includes either a MDPE or a blend of HDPE and LDPE.

The present invention provides methods of producing polyethylene films having high WVTR values, opacity, high stiffness and resistance to humidity. The films also have excellent  
15 deadfold characteristics which make them well suited for packaging of foods in bag-in-box operations conducted on vertical, form, fill and seal (VFFS) machinery. These properties make these films an excellent alternative to paper or cellophane in applications where high WVTR and insensitivity of film to moisture are required.

These and other advantages of the present invention will be appreciated from the detailed  
20 description and examples which are set forth herein. The detailed description and examples enhance the understanding of the invention, but are not intended to limit the scope of the invention.

Preferred embodiments of the invention have been chosen for purposes of illustration and description, but are not intended in any way to restrict the scope of the invention. The  
25 preferred embodiments of certain aspects of the invention are shown in the accompanying drawings, wherein:

FIG. 1 is a scanning electron micrograph showing a cross-sectional view of a conventional cavitated bioriented polypropylene film.

FIG. 2 is a scanning electron micrograph showing a cross-sectional view of a film prepared  
30 according to the present invention.

The present invention provides for bioriented polyethylene films having high WVTR and methods for producing the same. To practice the methods of the present invention, a polyethylene sheet is provided wherein at least one layer of a WVTR-controlling material is adherently superimposed to a core or base layer. The polyethylene sheet is then biaxially oriented resulting in a film having a desired WVTR. The resulting film has a base layer having a porous microstructure and a substantially higher WVTR than the desired WVTR for the film.

The base layer includes a polyethylene and a cavitating agent. Preferably, the polyethylene is a HDPE or a MDPE. The amount of polyethylene provided in the base layer prior to producing a film should be an amount sufficient to yield a base layer in the film having a thickness of from 0.5 mil to 2.0 mil, preferably 0.85 mil to 1.10 mil. It should be noted that any thickness value provided herein does not account for additional thickness resulting from cavitation.

As the term HDPE is used herein, it is defined to mean an ethylene-containing polymer having a density of 0.940 or higher. (Density (d) is expressed as  $\text{g/cm}^3$ .) One particularly suitable HDPE for use with the methods of the present invention is the resin sold as M6211 by Equistar. Another particularly suitable HDPE is the resin sold as HD 7845 by Exxon. Other suitable HDPE resins include, for example, BDM 94-25 available from Fina Oil and Chemical Co., Dallas, TX, and Sclair 19C and 19F available from Nova Corporation, Sarnia, Ontario, Canada.

The term "medium density polyethylene" (MDPE) as used herein is defined to mean an ethylene-containing polymer having a density of from 0.926 to 0.940. MDPE is readily available, e.g., Dowlex™ 2027A from The Dow Chemical Company, and Nova 74B and Nova 14G from Nova Corporation, Sarnia, Ontario, Canada.

As mentioned above, a cavitating agent is provided in the base layer. Such agents are typically added to the core or base layer prior to extrusion and are capable of generating voids (cavities) in the structure of the film during the film-making process. It is believed that small inhomogeneities introduced into the core layer by the cavitating agent result in points of weakness in the polyethylene sheet. The biaxial orienting step then induces tears in the core layer, causing cavitation in the processed film. The tears in the core layer vary in size and are



formed not only horizontally, i.e., within or parallel to the plane of the film, but also in the vertical dimension or perpendicular to the plane of the film.

Any suitable cavitating agent can be used. One especially preferred cavitant which can be used to practice the methods of the present invention is calcium carbonate ( $\text{CaCO}_3$ ). Other cavitating agents can also be used. Organic cavitating agents are also known, but are generally less preferred due to their limited operating temperature range. However, such organic cavitants can be useful if they are extremely finely divided and are either resistant to melting at operating temperatures or produce a suitable inhomogeneity in the polyethylene sheet. Cavitating agents can be included using methods known in the art, such as that described in application Serial No. 07/993,983. Accordingly, in the methods of the invention in which a cavitating agent is employed,  $\text{CaCO}_3$ , polyacrylate particulates, polystyrene or other cavitants can be included in the base layer.

The percentage of cavitating agent included in the base layer depends upon the desired WVTR. In particular, if a higher WVTR is desired, then more cavitating agent should be included in the base layer. Generally, the base layer can include from 1 wt.% to 30 wt.% of a cavitating agent. It is preferable, though, that the base layer include from 3 wt.% to 10 wt.% of a cavitating agent.

The WVTR-controlling layer includes a WVTR-controlling material. Any material that limits the WVTR in the resulting film can be used. Given the typically small dimensions of the WVTR-controlling layer, the WVTR-controlling material preferably should have a normalized WVTR (WVTR of 1 mil thick of film) lower than the normalized WVTR of the film, and substantially lower than the normalized WVTR of the cavitated polyethylene base layer. Preferred WVTR-controlling materials include MDPE or HDPE. The WVTR-controlling material can have a density as great as that of the polyethylene in the base layer, but it should not have a density greater than that of the polyethylene in the base layer. The amount of WVTR-controlling material included in the WVTR-controlling layer prior to adherently superimposing the WVTR-controlling layer to the base layer should be an amount sufficient to yield a WVTR-controlling layer in the film having a thickness of from 0.01 mil to 0.25 mil, preferably from 0.03 mil to 0.15 mil.

A film is produced by the methods of the present invention using conventional casting apparatus. For example, cast extrusion is generally accomplished using a standard multi-roll

stack system or a cast roll with an air cap (high velocity air applied to the outside of the sheet).

Other casting apparatus is also useful, such as a cast roll and water bath system.

A polyethylene film prepared according to the present invention is biaxially oriented. Biaxial orientation is employed to evenly distribute the strength qualities of a film in the longitudinal or "machine direction" (MD) of the film and in the lateral or "transverse direction" (TD) of the film. Biaxial oriented films tend to be stiffer and stronger, and also exhibit much better resistance to flexing and folding forces, leading to greater utility in packaging applications.

Biaxial orientation can be conducted simultaneously in both directions, however, most biaxial orientation processes use apparatus which stretches the film sequentially, first in one direction and then in the other. A typical apparatus will stretch a film in the MD first and then in the TD. The degree to which a film can be stretched is dependent upon factors including, for example, the polymer from which a film is made. For further discussion concerning high biorientation of polyethylene films, see U.S. Application Serial Nos. 08/715,546 and 08/940,261.

A film according to the present invention is made from polyethylene and can be stretched to a relatively high degree. In particular, a film can be stretched in the MD to a degree of from 5:1 to 8:1 and in the TD to a degree of from 6:1 to 15:1. Nevertheless, as a general rule with a film of this invention, the higher the degree of stretch in both the MD and the TD, the higher the WVTR in the resulting film. The temperature at which a film is biaxially oriented ("stretch temperature") can also influence the WVTR in the resulting film. As shown below in EXAMPLE 3, the WVTR of a resulting film can be increased by biaxially orienting a film at a lower stretch temperature.

Several embodiments of polyethylene films can be produced by the methods of the present invention. One exemplary embodiment of a film, which can be produced by the methods provided herein, has a base layer including HDPE and  $\text{CaCO}_3$ . The base layer is interposed between two WVTR-controlling layers, each of which includes MDPE. Sufficient amounts of HDPE,  $\text{CaCO}_3$  and WVTR-controlling material are provided prior to film production to yield a base layer of the film having a thickness from 0.85 mil to 1.10 mil and WVTR-controlling layers each having a thickness from 0.03 mil to 0.15 mil.

Another exemplary embodiment provides for a film having a base layer including MDPE and  $\text{CaCO}_3$ . The base layer is interposed between two WVTR-controlling layers and is coextensive with each of the WVTR-controlling layers. Further, a sufficient amount of MDPE and  $\text{CaCO}_3$  is provided prior to film production to yield a base layer of the film having a  
5 thickness from 0.85 mil to 1.10 mil and a sufficient amount of WVTR-controlling material should also be provided to yield WVTR-controlling layers each having a thickness from 0.03 mil to 0.15 mil. In addition, the WVTR-controlling layers can be of the same or different materials as desired. This film is preferable in some applications since it is less stiff and it creases less than films having a base layer including HDPE. In addition, this film has  
10 unidirectional tear properties in the machine direction.

Another exemplary embodiment provides for at least one tie layer interposed between a base layer and a WVTR-controlling layer wherein the tie layer is coextensive with each of the base layer and the WVTR-controlling layer. Additional tie layers can be provided to this structure to obtain a film having the desired WVTR. The tie layer of this embodiment includes  
15 MDPE or HDPE and the base layer includes HDPE and  $\text{CaCO}_3$ . Additionally, the tie layer can include pigment to provide color to the film and varying amounts of a cavitating agent to regulate the WVTR of the film.

Another exemplary embodiment is a five layer structure having a base layer, with first and second sides, interposed between two tie layers wherein one tie layer is interposed between  
20 the first side of the base layer and a first WVTR-controlling layer and the other tie layer is interposed between the second side of the base layer and a second WVTR-controlling layer. The tie layers of this structure are coextensive with the base layer and each of the WVTR-controlling layers is coextensive with its adjacent tie layer.

The base layer of this five layer structure includes HDPE and  $\text{CaCO}_3$  and the tie layers  
25 include MDPE or HDPE. Process conditions, though, can warrant using a tie layer including HDPE and  $\text{CaCO}_3$  if further cavitation is desired. In addition, the two tie layers can be of the same or different materials as desired. The WVTR-controlling layers of this structure include MDPE as the WVTR-controlling material. The result of biaxially orienting a sheet having this five layer structure is a rigid and opaque film having a gloss of 25% and paperlike  
30 characteristics.

Another exemplary embodiment also has a five layer structure having a base layer interposed between two tie layers wherein one tie layer is interposed between the first side of the base layer and a first WVTR-controlling layer and the other tie layer is interposed between the second side of the base layer and a second WVTR-controlling layer. The base layer of this layer structure includes HDPE and CaCO<sub>3</sub>. The tie layers of this structure include either a MDPE or a blend of HDPE and LDPE to assure good skin adhesion and can be of the same or different materials as desired. The WVTR-controlling material of the first and second WVTR-controlling layers of this structure includes an ethylene-propylene copolymer or an ethylene-propylene-butylene terpolymer. Further, the WVTR-controlling layers can be of the same or different materials as desired.

The result of biaxially orienting a sheet having this five layer structure where the WVTR-controlling material is an ethylene-propylene copolymer or an ethylene-propylene-butylene terpolymer, is a film having a high gloss typically greater than 50% (ASTM D 2457). In addition, the resulting five layer film is paperlike, opaque and rigid.

While these and other embodiments can be produced according to the methods of the present invention, it should be noted that several other film structures having multiple layers with varying compositions and thicknesses can be produced having a desired WVTR in accordance with the present invention.

The films of the present invention can be surface treated with conventional methods to improve wettability of the film and ink receptivity. Films can further be coated by known methods to modify barrier characteristics, provide heat seal properties and modify surface characteristics. The films can be modified by metallization to obtain a metal-like appearance and altered barrier characteristics. The films of the present invention are useful in numerous applications including food packaging and in particular, in food packaging where high WVTR is desirable such as the packaging of cheese products. Additionally, these films are advantageous for use in cigarette pack inner liners, as overwrap for butter, chocolate, candy, etc., and as twistwrap.

The following examples are provided to assist in further understanding the invention. The particular materials and conditions employed are intended to be further illustrative of the invention and are not limiting upon the reasonable scope thereof.

A series of experiments were performed to illustrate features and advantages of the present invention. Several of the manufacturing conditions were common to each case. For example, a polyethylene sheet was cast at a temperature between 160-180°F depending upon the thickness of the sheet, i.e., the caster temperature was higher for thicker sheets. In addition, orientation was performed using conventional orienting equipment in each case. Further, each film was stretched in the machine direction at a temperature 245-250°F and in the transverse direction at 262°F.

#### EXAMPLE 1

Referring now to Figures 1 and 2, cavitation of a film according to the present invention results in a surprising increase in the WVTR of the film. Figure 1 is a scanning electron micrograph showing a cross-section through a conventional cavitated bioriented polypropylene (OPP) film. The core layer of the film contains 5%  $\text{CaCO}_3$  as a cavitating agent. It is apparent that the cavitation introduced into this OPP film is exclusively within the plane defined by the film. Virtually no opening of the film in the dimension normal to the film plane (vertical) is evident. The physical structure of the cavitation in polypropylene is reflected in the minimal effect on the WVTR of the film. Typically, cavitation in OPP films increases WVTR by no more than 10%.

By contrast, Figure 2 is a scanning electron micrograph of a cross-section of a film prepared according to a method of the present invention. This film has a core layer of HDPE containing 5%  $\text{CaCO}_3$  as a cavitant. It is clear from Figure 2 that the cavitation introduced into the core layer includes not only the opening up in the film plane that is consistent with the cavitation observed in polypropylene, but also contains a significant and surprising degree of opening in the vertical dimension. This unexpected vertical opening in the film structure is observed to correlate with extraordinary increases in the WVTR of the core layer. It has been found that this feature of the films of the present invention permits selection of a wide range of WVTR values for the film by the process of providing one or more WVTR-controlling layers to limit net WVTR for the resulting film.

#### EXAMPLE 2

TABLE 1 shows a film structure produced by a method of the present invention. The film has an unexpectedly high WVTR of greater than 3.0 g/100inch<sup>2</sup> · day.

TABLE 1

	<u>Layers(from top to bottom)</u>	<u>Composition of Layer</u>	<u>Layer Thickness(mil)</u>
	Outer	MDPE	0.03
5	Tie	MDPE	0.10
	Core	HDPE + CaCO <sub>3</sub>	0.89
	Tie	HDPE + CaCO <sub>3</sub>	0.10
10	Outer	MDPE	0.03

It should be noted that the top side of this film structure is the caster side and the bottom side of the film structure is the airknife side. Also, the thickness of each layer does not account for any additional thickness resulting from cavitation.

The percentage of cavitant in the core layer and the tie layer on the airknife side of the film is 5 to 10% by weight of the layer. To increase the WVTR, more cavitant can be added to either or both layers containing cavitant. Additionally, cavitant can be added to the tie layer on the caster side of the film to increase the WVTR. This particular example includes MDPE in the tie layer on the caster side to reduce the WVTR.

The WVTR of a film can be increased or decreased by varying the physical conditions with respect to the film-making process. For example, reducing the thickness of non-cavitated layers increases the WVTR. Likewise, reducing the resin density of non-cavitated layers increases the WVTR of a film. The WVTR can also be increased by using lower stretch temperatures as shown in EXAMPLE 3 below or by using higher stretch ratios in the machine or transverse directions.

With respect to the resulting film of this example, the WVTR is much higher than anticipated. Other physical attributes of the film include a gloss of 25% (ASTM D 2457) and a light transmission ratio of 20% (ASTM 1003). The film thickness is 2.00 mil and the yield is 25,000 inch<sup>2</sup>/lb.

### EXAMPLE 3

The film structures described in TABLE II show that WVTR increases when stretching is performed at lower temperatures and when structures are more cavitated.

TABLE II

	<u>Sample</u>	<u>Layer 1</u>	<u>Layer 2</u>	<u>Layer 3</u>	<u>Layer 4</u>	<u>Layer 5</u>	<u>WVTR</u>
5	1	0.03 MDPE	0.10 HDPE	0.89 HDPE + 7% CaCO <sub>3</sub>	0.10 HDPE	0.03 MDPE	1.00
	2	0.03 MDPE	0.10 HDPE	0.89 HDPE + 7% CaCO <sub>3</sub>	0.10 HDPE	0.03 MDPE	2.05
10	3	0.03 MDPE	0.10 HDPE	0.89 HDPE + 7% CaCO <sub>3</sub>	0.10 HDPE	0.03 MDPE	0.88
	4	0.03 MDPE	0.10 MDPE	0.89 HDPE + 7% CaCO <sub>3</sub>	0.10 HDPE + 7% CaCO <sub>3</sub>	0.03 MDPE	2.93
15	5	0.03 MDPE	0.10 HDPE + 7% CaCO <sub>3</sub>	0.89 HDPE + 7% CaCO <sub>3</sub>	0.10 HDPE + 7% CaCO <sub>3</sub>	0.03 MDPE	14.1
20	6	0.03 EP Copolymer	0.10 MDPE	0.89 HDPE + 7% CaCO <sub>3</sub>	0.10 MDPE	0.03 EP Copolymer	2.67- 4.12

The thickness of the HDPE and MDPE layers is expressed above in mils and does not take into account additional thickness resulting from cavitation. In addition, the WVTR is expressed above in g/100inch<sup>2</sup>·day.

Samples 1 and 3 were produced under similar conditions to establish a constant WVTR for comparison with WVTR values resulting from different physical conditions. Sample 2 was produced at a stretch temperature of 3°F lower than that of Sample 1. Comparing the WVTR of Samples 1 and 3 with that of Sample 2, it is readily apparent that a lower stretch temperature caused an increase in the WVTR of Sample 2.

Sample 4 was produced at conditions similar to Samples 1 and 3 except that layer 4 of Sample 4 was cavitated. The resulting increase in WVTR in Sample 4 compared to those of Samples 1 and 3 indicates that WVTR increases as a film is more cavitated.

The result in Sample 5 further supports the assertion drawn from the comparison of Sample 4 to Samples 1 and 3. In particular, tie layers 2 and 4 of Sample 5 were cavitated and the resulting WVTR was much higher than the WVTR of Samples 1 and 3. Clearly, increasing the cavitation of a film results in higher WVTR values.

Sample 6 shows a film structure wherein an ethylene-propylene copolymer is substituted for MDPE in the WVTR-controlling layers. This film has a higher WVTR in comparison to Samples 1 and 3 and it also has a high gloss of 61%.

**EXAMPLE 4**

TABLE III shows three layer film structures resulting from process conditions different than those used in obtaining the results of TABLE II. In particular, the results of TABLE III show that WVTR increases as cavitation increases regardless of what cavitant is used.

5

**TABLE III**

	<u>Sample</u>	<u>Layer 1</u>	<u>Layer 2</u>	<u>Layer 3</u>	<u>WVTR</u>
10	7	0.17 MDPE	0.81 HDPE (M6211 Resin)	0.17 MDPE	0.2
	8	0.17 MDPE	0.81 HDPE + 7% CaCO <sub>3</sub>	0.17 MDPE	4.0
15	9	0.17 MDPE	0.81 HDPE + 7% CaCO <sub>3</sub>	0.17 MDPE	7.2
20	10	0.17 MDPE	0.81 HDPE + 7% Epostar MA1002	0.17 MDPE	5.2

The thickness of the HDPE and MDPE layers is expressed above in mils and does not take into account additional thickness resulting from cavitation. In addition, the WVTR is expressed above in g/100inch<sup>2</sup> · day.

25 Sample 7 can be compared to Samples 8-10 to prove that cavitation increases the WVTR of a film. In particular, Sample 7 which is not cavitated had a resulting WVTR of 0.2 g/100inch<sup>2</sup> · day whereas Samples 8-10 which each had a cavitated core layer had resulting WVTRs of 4.0 g/100inch<sup>2</sup> · day, 7.2 g/100inch<sup>2</sup> · day and 5.2 g/100inch<sup>2</sup> · day, respectively.

30 Sample 10 is comparable to Samples 8 and 9 to illustrate that cavitating agents other than calcium carbonate (CaCO<sub>3</sub>) can be used to obtain similar results. In particular, Epostar MA 1002 was used as the cavitating agent in Sample 10. The resulting WVTR of 5.2 g/100inch<sup>2</sup> · day in Sample 10 supports the notion that cavitating agents other than calcium carbonate (CaCO<sub>3</sub>) can be used with the polyethylene films of the present invention.



**CLAIMS:**

1. A polyethylene film comprising:
  - (a) a base layer comprising polyethylene and a cavitating agent, said base layer
  - 5 having a first side and a second side; and
  - (b) at least one layer of a water vapor transmission rate (WVTR)-controlling material coextensive with one of said sides of said base layer;whereby said polyethylene film has a desired WVTR, wherein said base layer has a porous microstructure and a WVTR substantially higher than the desired WVTR for said polyethylene
- 10 film.
2. A polyethylene film according to Claim 1, which further comprises at least one tie layer interposed between said base layer and said WVTR-controlling layer and coextensive with each of said base layer and said WVTR-controlling layer.
- 15
3. A polyethylene film according to Claim 2, wherein said WVTR-controlling layer comprises an ethylene-propylene copolymer or an ethylene-propylene-butylene terpolymer, and each tie layer comprises a polyethylene comprising medium density polyethylene (MDPE) or a blend of high density polyethylene (HDPE) and low density polyethylene (LDPE).
- 20
4. A polyethylene film according to Claim 1, which further comprises a second layer of WVTR-controlling material coextensive with the other side of said base layer.
5. A polyethylene film according to Claim 4, wherein:
  - 25 a first tie layer is interposed between said base layer and said first WVTR-controlling layer, coextensive with each of said base layer and said first WVTR-controlling layer, and
  - a second tie layer is interposed between said base layer and said second WVTR-controlling layer, coextensive with each of said base layer and said second WVTR-controlling
  - 30 layer.

6. A polyethylene film according to Claim 1, wherein said WVTR-controlling material is a medium density polyethylene (MDPE) or a high density polyethylene (HDPE) having a density no greater than that of said polyethylene in said base layer.

5 7. A polyethylene film according to Claim 1, wherein said WVTR-controlling layer has a thickness of from 0.03 mil (3 gauge) to 0.15 mil (15 gauge).

8. A polyethylene film according to Claim 1, wherein said base layer has a thickness of from 0.5 mil (50 gauge) to 2.0 mil (200 gauge).

10

9. A method of producing a polyethylene film having a desired water vapor transmission rate (WVTR), comprising:

(a) adherently superimposing at least one layer of a WVTR-controlling material coextensively to a first side of a base layer having first and second sides; and

15 (b) biaxially orienting the composite polyethylene sheet resulting from step (a); whereby there is provided said polyethylene film having the desired WVTR, wherein said base layer has a porous microstructure and a WVTR substantially higher than the desired WVTR for said polyethylene film.

20 10. A method according to Claim 9, wherein step (a) comprises providing at least one tie layer interposed between said base layer and said WVTR-controlling layer and coextensive with each of said base layer and said WVTR-controlling layer.

1/1

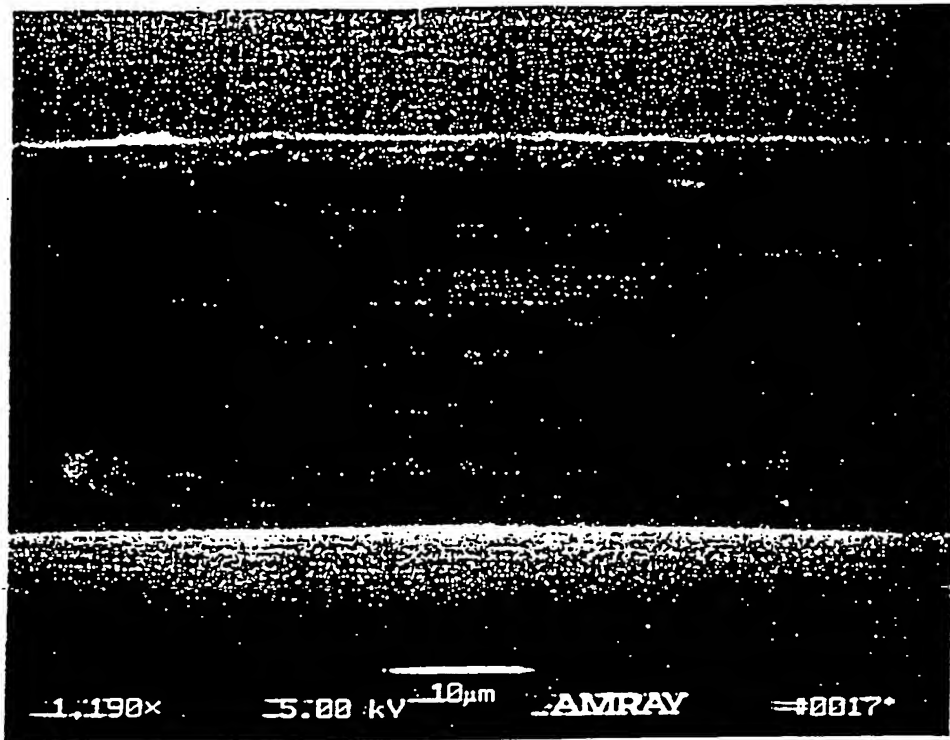


FIG. 1



FIG. 2

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/19788

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>														
IPC(6) :B32B 5/28, 27/32														
US CL :Please See Extra Sheet.														
According to International Patent Classification (IPC) or to both national classification and IPC														
<b>B. FIELDS SEARCHED</b>														
Minimum documentation searched (classification system followed by classification symbols)														
U.S. : 428/ 213, 317.9 319.7, 319.9, 515, 516 and 264/ 41, 290.2, 172.19, 172.19														
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched														
NONE														
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)														
WEST: core same (polyethylene and void\$ and particle\$), (stretch\$ or orient\$).														
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>														
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.												
X,P	US 5,885,721 A (SU et al.) 23 March 1999, see the entire document especially column 7, lines 54-64; column 8, line 61 to column 9, line 6; column 11, lines 60+; column 12, lines 36-51; column 14, lines 19-49; column 16, lines 64-67; and claims 1 and 6.	1-10												
X	US 4,713,273 A (FREEDMAN) 15 December 1987, see the entire document especially figures 1 and 2; column 9, lines 65+; column 10, lines 1-58. See also column 3, lines 3+.	1-10												
A	US 5,176,954 A (KELLER et al.) 5 January 1993, see the entire document especially example 8.	1-10												
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.														
<table border="0"> <tr> <td>* Special categories of cited documents:</td> <td>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>*A* document defining the general state of the art which is not considered to be of particular relevance</td> <td>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>*E* earlier document published on or after the international filing date</td> <td>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>*a* document member of the same patent family</td> </tr> <tr> <td>*O* document referring to an oral disclosure, use, exhibition or other means</td> <td></td> </tr> <tr> <td>*P* document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </table>			* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*a* document member of the same patent family	*O* document referring to an oral disclosure, use, exhibition or other means		*P* document published prior to the international filing date but later than the priority date claimed	
* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention													
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone													
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*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*a* document member of the same patent family													
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Date of the actual completion of the international search		Date of mailing of the international search report												
18 NOVEMBER 1999		23 DEC 1999												
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer D. LAWRENCE TARAZANO Telephone No. (703) 308-0651												

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US99/19788

**A. CLASSIFICATION OF SUBJECT MATTER:**

**US CL :**

**428/ 213, 317.9 319.7, 319.9, 515, 516 and 264/ 41, 290.2, 172.19, 172.19**

CORRECTED VERSION

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
9 March 2000 (09.03.2000)

PCT

(10) International Publication Number  
**WO 00/12302 A1**

- (51) International Patent Classification<sup>6</sup>: B32B 5/28, 27/32 (81) Designated States (*national*): AU, BR, CA, CN, ID, JP, KR, SG, VN.
- (21) International Application Number: PCT/US99/19788
- (22) International Filing Date: 27 August 1999 (27.08.1999) (84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
09/145,949 2 September 1998 (02.09.1998) US
- (71) Applicant: MOBIL OIL CORPORATION [US/US];  
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- (74) Agent: ALEXANDER, David, J.; ExxonMobile Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US).
- Published:  
— With international search report.
- (48) Date of publication of this corrected version:  
22 March 2001
- (15) Information about Correction:  
see PCT Gazette No. 12/2001 of 22 March 2001, Section II

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: BIORIENTED POLYETHYLENE FILM WITH A HIGH WATER VAPOR TRANSMISSION RATE

(57) Abstract: Polyethylene films having desired water vapor transmission rates (WVTR) and methods of producing the same are provided. The methods include adherently superimposing at least one layer of a WVTR-controlling material to a base layer including a polyethylene and a cavitating agent, and subsequently biaxially orienting the composite polyethylene sheet to yield a film having the desired WVTR. The base layer has a porous microstructure and a WVTR substantially higher than the desired WVTR.

WO 00/12302 A1

**BIORIENTED POLYETHYLENE FILM  
WITH A HIGH WATER VAPOR TRANSMISSION RATE**

The present invention relates to polymer films and methods for preparing polymer films.  
5 Specifically, the present invention relates to bioriented polyethylene films having high water vapor transmission rates (WVTR) and methods of preparing the same.

Generally, in the preparation of a film from granular or pelleted polymer resin, the polymer is first extruded to provide a stream of polymer melt, and then the extruded polymer is subjected to the film-making process. Film-making typically involves a number of discrete  
10 procedural stages, including melt film formation, quenching, and windup. For a general description of these and other processes associated with film-making, see KR Osborn and WA Jenkins, *Plastic Films: Technology and Packaging Applications*, Technomic Publishing Co., Inc., Lancaster, Pennsylvania (1992).

An optional part of the film-making process is a procedure known as "orientation." The  
15 "orientation" of a polymer is a reference to its molecular organization, i.e., the orientation of molecules relative to each other. Similarly, the process of "orientation" is the process by which directionality (orientation) is imposed upon the polymeric arrangements in the film. The process of orientation is employed to impart desirable properties to films, including making cast films tougher (higher tensile properties). Depending on whether the film is made by  
20 casting as a flat film or by blowing as a tubular film, the orientation process requires substantially different procedures. This is related to the different physical characteristics possessed by films made by the two conventional film-making processes: casting and blowing. Generally, blown films tend to have greater stiffness, toughness and barrier properties. By contrast, cast films usually have the advantages of greater film clarity and uniformity of  
25 thickness and flatness, generally permitting use of a wider range of polymers and producing a higher quality film.

Orientation is accomplished by heating a polymer to a temperature at or above its glass-transition temperature ( $T_g$ ) but below its crystalline melting point ( $T_m$ ), and then stretching the film quickly. On cooling, the molecular alignment imposed by the stretching competes  
30 favorably with crystallization and the drawn polymer molecules condense into a crystalline network with crystalline domains (crystallites) aligned in the direction of the drawing force.

As a general rule, the degree of orientation is proportional to the amount of stretch, and inversely related to the temperature at which the stretching is performed. For example, if a base material is stretched to twice its original length (2:1) at a higher temperature, the orientation in the resulting film will tend to be less than that in another film stretched 2:1 but at  
5 a lower temperature. Moreover, higher orientation also generally correlates with a higher modulus, i.e., measurably higher stiffness and strength. Further, as a general rule, higher orientation correlates with lower WVTR values for films.

Previously, high WVTR values have been difficult to achieve with polyolefin films. Typically, film production methods aim to lower WVTR values for polyolefin films. As such,  
10 polyolefin films inherently have low WVTR values compared to traditional wrapping materials such as cellulose films or paper.

Accordingly, it is one of the purposes of this invention, among others, to produce bioriented polyethylene films having high WVTR values, by providing an economical and relatively uncomplicated method of making polyethylene films that imparts superior  
15 characteristics to the films, without requirement for chemical additives such as cross-linking agents, and without requirement for supplemental processing steps such as irradiation of the film.

It has now been discovered that these and other purposes can be achieved by the present invention, which provides for bioriented polyethylene films having high WVTR values and  
20 methods of producing the same.

Various structured polyethylene films having high WVTR can be produced by the methods of the present invention. One embodiment of the present invention provides for a film having a base layer and at least one layer of a WVTR controlling material whereby the polyethylene film has a desired WVTR and the base layer has a porous microstructure and WVTR  
25 substantially higher than the desired WVTR for the polyethylene film. The base layer includes polyethylene and a cavitating agent, and preferably, the polyethylene is a medium density polyethylene (MDPE) or a high density polyethylene (HDPE). The base layer also has a first side and a second side. Further, the base layer preferably has a thickness of from 0.5 mil to 2.0 mil (1 mil = 0.001 inch = 100 gauge). It should be noted that any thickness value provided  
30 herein does not account for additional thickness resulting from cavitation.



The WVTR-controlling layer of the polyethylene film is coextensive with one of the sides of the base layer and includes a WVTR-controlling material, either a MDPE or a HDPE, which should not have a density greater than that of the polyethylene in the base layer. Further, it is preferable that the WVTR-controlling layer have a thickness of from 0.03 mil (3  
5 gauge) to 0.15 mil (15 gauge).

A preferred embodiment of the present invention provides for a film having the desired WVTR and having a tie layer interposed between a base layer and a WVTR-controlling layer wherein the tie layer is coextensive with each of the base layer and the WVTR-controlling layer. The base layer, which includes polyethylene and a cavitating agent, has a first side and a  
10 second side. Further, the base layer has a porous microstructure and a WVTR substantially higher than the desired WVTR for the polyethylene film. Preferably, the WVTR-controlling layer includes a WVTR-controlling material of either MDPE or HDPE. Alternatively, the WVTR-controlling material can be either an ethylene-propylene copolymer or an ethylene-propylene-butylene terpolymer wherein the tie layer would be either a MDPE or a blend of  
15 HDPE and low density polyethylene (LDPE).

Another preferred embodiment of the present invention provides for a film having the desired WVTR wherein the film has first and second layers of a WVTR-controlling material coextensive with the first and second sides of the base layer. The base layer, which includes polyethylene and a cavitating agent, has a porous microstructure and a WVTR substantially  
20 higher than the desired WVTR for the polyethylene film. The first and second WVTR-controlling layers should each include a WVTR-controlling material of preferably either a MDPE or a HDPE.

Another preferred embodiment of the present invention provides for a film wherein a first tie layer is interposed between a base layer and a first WVTR-controlling layer and a second  
25 tie layer is interposed between the base layer and a second WVTR-controlling layer. The first tie layer is coextensive with each of the base layer and first WVTR-controlling layer and the second tie layer is coextensive with each of the base layer and the second WVTR-controlling layer.

It should be noted that polyethylene films according to the present invention are not  
30 limited to the foregoing structures and can include several layers as a plurality of WVTR-controlling layers or tie layers can be provided to obtain a film having the desired WVTR.

The methods of the present invention provide for adherently superimposing at least one layer of a WVTR-controlling material coextensively to a first side of a base layer having first and second sides and then biaxially orienting the composite polyethylene sheet to obtain a film having a desired WVTR. The base layer of the composite polyethylene sheet includes  
5 polyethylene and a cavitating agent. The composite polyethylene sheet is biaxially oriented whereby there is provided a bioriented polyethylene film having the desired WVTR and whereby the base layer has a porous microstructure and a WVTR substantially higher than the desired WVTR.

Preferably, the polyethylene of the base layer is a MDPE or a HDPE. Further, it is  
10 preferable that the amount of polyethylene provided in the base layer prior to producing a film be an amount sufficient to yield a base layer in the film having a thickness of from 0.5 mil to 2.0 mil. It should be noted that any thickness value provided herein does not account for additional thickness resulting from cavitation. In addition, it is preferable that the WVTR-controlling material is a MDPE or a HDPE, however, the WVTR-controlling material  
15 should not have a density greater than that of the polyethylene in the base layer. Further, it is preferable that the WVTR-controlling material is provided in an amount sufficient to yield a WVTR-controlling layer in the film having a thickness of from 0.03 mil to 0.15 mil.

A preferred method of the present invention provides for producing a film having a three layer structure. In particular, a first layer of a WVTR-controlling material is adherently  
20 superimposed to a first side of a base layer and a second layer of a WVTR-controlling material is adherently superimposed to the second side of the base layer. The composite polyethylene sheet is then biaxially oriented.

Another preferred method of the present invention provides for producing a film having a five layer structure. In particular, a base layer having first and second sides is provided and is  
25 interposed between two tie layers wherein the first tie layer is interposed between the first side of the base layer and a first WVTR-controlling layer, and wherein the second tie layer is interposed between the second side of the base layer and a second WVTR-controlling layer. The tie layers are each adherently superimposed to the base layer and are each coextensive with the base layer. The WVTR-controlling layers are each adherently superimposed to the tie  
30 layers and are each coextensive with their adjacent tie layer. The composite polyethylene

sheet is then biaxially oriented. The tie layers of this structure include MDPE or HDPE and can also include a cavitating agent to regulate the WVTR.

Another method of the present invention provides for producing a film by adherently superimposing at least one tie layer to a base layer wherein the tie layer is coextensive with the  
5 base layer, and further, adherently superimposing a WVTR-controlling layer to the tie layer wherein the WVTR-controlling layer is coextensive with the tie layer. The WVTR-controlling layer comprises a WVTR-controlling material of preferably HDPE or MDPE. The tie layer includes MDPE or HDPE and can also include a cavitating agent to regulate the WVTR. However, an alternative method includes provision for a WVTR-controlling layer including a  
10 WVTR-controlling material of either an ethylene-propylene copolymer or an ethylene-propylene-butylene terpolymer wherein the tie layer includes either a MDPE or a blend of HDPE and LDPE.

The present invention provides methods of producing polyethylene films having high WVTR values, opacity, high stiffness and resistance to humidity. The films also have excellent  
15 deadfold characteristics which make them well suited for packaging of foods in bag-in-box operations conducted on vertical, form, fill and seal (VFFS) machinery. These properties make these films an excellent alternative to paper or cellophane in applications where high WVTR and insensitivity of film to moisture are required.

These and other advantages of the present invention will be appreciated from the detailed  
20 description and examples which are set forth herein. The detailed description and examples enhance the understanding of the invention, but are not intended to limit the scope of the invention.

Preferred embodiments of the invention have been chosen for purposes of illustration and description, but are not intended in any way to restrict the scope of the invention. The  
25 preferred embodiments of certain aspects of the invention are shown in the accompanying drawings, wherein:

FIG. 1 is a scanning electron micrograph showing a cross-sectional view of a conventional cavitated bioriented polypropylene film.

FIG. 2 is a scanning electron micrograph showing a cross-sectional view of a film prepared  
30 according to the present invention.

The present invention provides for bioriented polyethylene films having high WVTR and methods for producing the same. To practice the methods of the present invention, a polyethylene sheet is provided wherein at least one layer of a WVTR-controlling material is adherently superimposed to a core or base layer. The polyethylene sheet is then biaxially oriented resulting in a film having a desired WVTR. The resulting film has a base layer having a porous microstructure and a substantially higher WVTR than the desired WVTR for the film.

The base layer includes a polyethylene and a cavitating agent. Preferably, the polyethylene is a HDPE or a MDPE. The amount of polyethylene provided in the base layer prior to producing a film should be an amount sufficient to yield a base layer in the film having a thickness of from 0.5 mil to 2.0 mil, preferably 0.85 mil to 1.10 mil. It should be noted that any thickness value provided herein does not account for additional thickness resulting from cavitation.

As the term HDPE is used herein, it is defined to mean an ethylene-containing polymer having a density of 0.940 or higher. (Density (d) is expressed as  $\text{g/cm}^3$ .) One particularly suitable HDPE for use with the methods of the present invention is the resin sold as M6211 by Equistar. Another particularly suitable HDPE is the resin sold as HD 7845 by Exxon. Other suitable HDPE resins include, for example, BDM 94-25 available from Fina Oil and Chemical Co., Dallas, TX, and Sclair 19C and 19F available from Nova Corporation, Sarnia, Ontario, Canada.

The term "medium density polyethylene" (MDPE) as used herein is defined to mean an ethylene-containing polymer having a density of from 0.926 to 0.940. MDPE is readily available, e.g., Dowlex™ 2027A from The Dow Chemical Company, and Nova 74B and Nova 14G from Nova Corporation, Sarnia, Ontario, Canada.

As mentioned above, a cavitating agent is provided in the base layer. Such agents are typically added to the core or base layer prior to extrusion and are capable of generating voids (cavities) in the structure of the film during the film-making process. It is believed that small inhomogeneities introduced into the core layer by the cavitating agent result in points of weakness in the polyethylene sheet. The biaxial orienting step then induces tears in the core layer, causing cavitation in the processed film. The tears in the core layer vary in size and are

formed not only horizontally, i.e., within or parallel to the plane of the film, but also in the vertical dimension or perpendicular to the plane of the film.

Any suitable cavitating agent can be used. One especially preferred cavitant which can be used to practice the methods of the present invention is calcium carbonate ( $\text{CaCO}_3$ ). Other  
5 cavitating agents can also be used. Organic cavitating agents are also known, but are generally less preferred due to their limited operating temperature range. However, such organic cavitants can be useful if they are extremely finely divided and are either resistant to melting at operating temperatures or produce a suitable inhomogeneity in the polyethylene sheet. Cavitating agents can be included using methods known in the art, such as that  
10 described in application Serial No. 07/993,983. Accordingly, in the methods of the invention in which a cavitating agent is employed,  $\text{CaCO}_3$ , polyacrylate particulates, polystyrene or other cavitants can be included in the base layer.

The percentage of cavitating agent included in the base layer depends upon the desired WVTR. In particular, if a higher WVTR is desired, then more cavitating agent should be  
15 included in the base layer. Generally, the base layer can include from 1 wt.% to 30 wt.% of a cavitating agent. It is preferable, though, that the base layer include from 3 wt.% to 10 wt.% of a cavitating agent.

The WVTR-controlling layer includes a WVTR-controlling material. Any material that limits the WVTR in the resulting film can be used. Given the typically small dimensions of the  
20 WVTR-controlling layer, the WVTR-controlling material preferably should have a normalized WVTR (WVTR of 1 mil thick of film) lower than the normalized WVTR of the film, and substantially lower than the normalized WVTR of the cavitated polyethylene base layer. Preferred WVTR-controlling materials include MDPE or HDPE. The WVTR-controlling material can have a density as great as that of the polyethylene in the base layer, but it should  
25 not have a density greater than that of the polyethylene in the base layer. The amount of WVTR-controlling material included in the WVTR-controlling layer prior to adherently superimposing the WVTR-controlling layer to the base layer should be an amount sufficient to yield a WVTR-controlling layer in the film having a thickness of from 0.01 mil to 0.25 mil, preferably from 0.03 mil to 0.15 mil.

30 A film is produced by the methods of the present invention using conventional casting apparatus. For example, cast extrusion is generally accomplished using a standard multi-roll

stack system or a cast roll with an air cap (high velocity air applied to the outside of the sheet).

Other casting apparatus is also useful, such as a cast roll and water bath system.

A polyethylene film prepared according to the present invention is biaxially oriented.

Biaxial orientation is employed to evenly distribute the strength qualities of a film in the

5 longitudinal or "machine direction" (MD) of the film and in the lateral or "transverse direction" (TD) of the film. Biaxial oriented films tend to be stiffer and stronger, and also exhibit much better resistance to flexing and folding forces, leading to greater utility in packaging applications.

Biaxial orientation can be conducted simultaneously in both directions, however, most  
10 biaxial orientation processes use apparatus which stretches the film sequentially, first in one direction and then in the other. A typical apparatus will stretch a film in the MD first and then in the TD. The degree to which a film can be stretched is dependent upon factors including, for example, the polymer from which a film is made. For further discussion concerning high biorientation of polyethylene films, see U.S. Application Serial Nos. 08/715,546 and  
15 08/940,261.

A film according to the present invention is made from polyethylene and can be stretched to a relatively high degree. In particular, a film can be stretched in the MD to a degree of from 5:1 to 8:1 and in the TD to a degree of from 6:1 to 15:1. Nevertheless, as a general rule with a film of this invention, the higher the degree of stretch in both the MD and the TD, the higher  
20 the WVTR in the resulting film. The temperature at which a film is biaxially oriented ("stretch temperature") can also influence the WVTR in the resulting film. As shown below in EXAMPLE 3, the WVTR of a resulting film can be increased by biaxially orienting a film at a lower stretch temperature.

Several embodiments of polyethylene films can be produced by the methods of the present  
25 invention. One exemplary embodiment of a film, which can be produced by the methods provided herein, has a base layer including HDPE and  $\text{CaCO}_3$ . The base layer is interposed between two WVTR-controlling layers, each of which includes MDPE. Sufficient amounts of HDPE,  $\text{CaCO}_3$  and WVTR-controlling material are provided prior to film production to yield a base layer of the film having a thickness from 0.85 mil to 1.10 mil and WVTR-controlling  
30 layers each having a thickness from 0.03 mil to 0.15 mil.

Another exemplary embodiment provides for a film having a base layer including MDPE and  $\text{CaCO}_3$ . The base layer is interposed between two WVTR-controlling layers and is coextensive with each of the WVTR-controlling layers. Further, a sufficient amount of MDPE and  $\text{CaCO}_3$  is provided prior to film production to yield a base layer of the film having a thickness from 0.85 mil to 1.10 mil and a sufficient amount of WVTR-controlling material should also be provided to yield WVTR-controlling layers each having a thickness from 0.03 mil to 0.15 mil. In addition, the WVTR-controlling layers can be of the same or different materials as desired. This film is preferable in some applications since it is less stiff and it creases less than films having a base layer including HDPE. In addition, this film has unidirectional tear properties in the machine direction.

Another exemplary embodiment provides for at least one tie layer interposed between a base layer and a WVTR-controlling layer wherein the tie layer is coextensive with each of the base layer and the WVTR-controlling layer. Additional tie layers can be provided to this structure to obtain a film having the desired WVTR. The tie layer of this embodiment includes MDPE or HDPE and the base layer includes HDPE and  $\text{CaCO}_3$ . Additionally, the tie layer can include pigment to provide color to the film and varying amounts of a cavitating agent to regulate the WVTR of the film.

Another exemplary embodiment is a five layer structure having a base layer, with first and second sides, interposed between two tie layers wherein one tie layer is interposed between the first side of the base layer and a first WVTR-controlling layer and the other tie layer is interposed between the second side of the base layer and a second WVTR-controlling layer. The tie layers of this structure are coextensive with the base layer and each of the WVTR-controlling layers is coextensive with its adjacent tie layer.

The base layer of this five layer structure includes HDPE and  $\text{CaCO}_3$  and the tie layers include MDPE or HDPE. Process conditions, though, can warrant using a tie layer including HDPE and  $\text{CaCO}_3$  if further cavitation is desired. In addition, the two tie layers can be of the same or different materials as desired. The WVTR-controlling layers of this structure include MDPE as the WVTR-controlling material. The result of biaxially orienting a sheet having this five layer structure is a rigid and opaque film having a gloss of 25% and paperlike characteristics.

Another exemplary embodiment also has a five layer structure having a base layer interposed between two tie layers wherein one tie layer is interposed between the first side of the base layer and a first WVTR-controlling layer and the other tie layer is interposed between the second side of the base layer and a second WVTR-controlling layer. The base layer of this  
5 layer structure includes HDPE and  $\text{CaCO}_3$ . The tie layers of this structure include either a MDPE or a blend of HDPE and LDPE to assure good skin adhesion and can be of the same or different materials as desired. The WVTR-controlling material of the first and second WVTR-controlling layers of this structure includes an ethylene-propylene copolymer or an ethylene-propylene-butylene terpolymer. Further, the WVTR-controlling layers can be of the same or  
10 different materials as desired.

The result of biaxially orienting a sheet having this five layer structure where the WVTR-controlling material is an ethylene-propylene copolymer or an ethylene-propylene-butylene terpolymer, is a film having a high gloss typically greater than 50% (ASTM D 2457). In addition, the resulting five layer film is paperlike, opaque and rigid.

15 While these and other embodiments can be produced according to the methods of the present invention, it should be noted that several other film structures having multiple layers with varying compositions and thicknesses can be produced having a desired WVTR in accordance with the present invention.

The films of the present invention can be surface treated with conventional methods to  
20 improve wettability of the film and ink receptivity. Films can further be coated by known methods to modify barrier characteristics, provide heat seal properties and modify surface characteristics. The films can be modified by metallization to obtain a metal-like appearance and altered barrier characteristics. The films of the present invention are useful in numerous applications including food packaging and in particular, in food packaging where high WVTR  
25 is desirable such as the packaging of cheese products. Additionally, these films are advantageous for use in cigarette pack inner liners, as overwrap for butter, chocolate, candy, etc., and as twistwrap.

The following examples are provided to assist in further understanding the invention. The particular materials and conditions employed are intended to be further illustrative of the  
30 invention and are not limiting upon the reasonable scope thereof.



A series of experiments were performed to illustrate features and advantages of the present invention. Several of the manufacturing conditions were common to each case. For example, a polyethylene sheet was cast at a temperature between 160-180°F depending upon the thickness of the sheet, i.e., the caster temperature was higher for thicker sheets. In addition, orientation was performed using conventional orienting equipment in each case. Further, each film was stretched in the machine direction at a temperature 245-250°F and in the transverse direction at 262°F.

### EXAMPLE 1

Referring now to Figures 1 and 2, cavitation of a film according to the present invention results in a surprising increase in the WVTR of the film. Figure 1 is a scanning electron micrograph showing a cross-section through a conventional cavitated bioriented polypropylene (OPP) film. The core layer of the film contains 5%  $\text{CaCO}_3$  as a cavitating agent. It is apparent that the cavitation introduced into this OPP film is exclusively within the plane defined by the film. Virtually no opening of the film in the dimension normal to the film plane (vertical) is evident. The physical structure of the cavitation in polypropylene is reflected in the minimal effect on the WVTR of the film. Typically, cavitation in OPP films increases WVTR by no more than 10%.

By contrast, Figure 2 is a scanning electron micrograph of a cross-section of a film prepared according to a method of the present invention. This film has a core layer of HDPE containing 5%  $\text{CaCO}_3$  as a cavitant. It is clear from Figure 2 that the cavitation introduced into the core layer includes not only the opening up in the film plane that is consistent with the cavitation observed in polypropylene, but also contains a significant and surprising degree of opening in the vertical dimension. This unexpected vertical opening in the film structure is observed to correlate with extraordinary increases in the WVTR of the core layer. It has been found that this feature of the films of the present invention permits selection of a wide range of WVTR values for the film by the process of providing one or more WVTR-controlling layers to limit net WVTR for the resulting film.

### EXAMPLE 2

TABLE 1 shows a film structure produced by a method of the present invention. The film has an unexpectedly high WVTR of greater than 3.0 g/100inch<sup>2</sup> · day.

TABLE 1

	<u>Layers(from top to bottom)</u>	<u>Composition of Layer</u>	<u>Layer Thickness(mil)</u>
	Outer	MDPE	0.03
5	Tie	MDPE	0.10
	Core	HDPE + CaCO <sub>3</sub>	0.89
	Tie	HDPE + CaCO <sub>3</sub>	0.10
10	Outer	MDPE	0.03

It should be noted that the top side of this film structure is the caster side and the bottom side of the film structure is the airknife side. Also, the thickness of each layer does not account for any additional thickness resulting from cavitation.

The percentage of cavitant in the core layer and the tie layer on the airknife side of the film is 5 to 10% by weight of the layer. To increase the WVTR, more cavitant can be added to either or both layers containing cavitant. Additionally, cavitant can be added to the tie layer on the caster side of the film to increase the WVTR. This particular example includes MDPE in the tie layer on the caster side to reduce the WVTR.

The WVTR of a film can be increased or decreased by varying the physical conditions with respect to the film-making process. For example, reducing the thickness of non-cavitated layers increases the WVTR. Likewise, reducing the resin density of non-cavitated layers increases the WVTR of a film. The WVTR can also be increased by using lower stretch temperatures as shown in EXAMPLE 3 below or by using higher stretch ratios in the machine or transverse directions.

With respect to the resulting film of this example, the WVTR is much higher than anticipated. Other physical attributes of the film include a gloss of 25% (ASTM D 2457) and a light transmission ratio of 20% (ASTM 1003). The film thickness is 2.00 mil and the yield is 25,000 inch<sup>2</sup>/lb.

### EXAMPLE 3

The film structures described in TABLE II show that WVTR increases when stretching is performed at lower temperatures and when structures are more cavitated.

TABLE II

	<u>Sample</u>	<u>Layer 1</u>	<u>Layer 2</u>	<u>Layer 3</u>	<u>Layer 4</u>	<u>Layer 5</u>	<u>WVTR</u>
5	1	0.03 MDPE	0.10 HDPE	0.89 HDPE + 7% CaCO <sub>3</sub>	0.10 HDPE	0.03 MDPE	1.00
	2	0.03 MDPE	0.10 HDPE	0.89 HDPE + 7% CaCO <sub>3</sub>	0.10 HDPE	0.03 MDPE	2.05
10	3	0.03 MDPE	0.10 HDPE	0.89 HDPE + 7% CaCO <sub>3</sub>	0.10 HDPE	0.03 MDPE	0.88
15	4	0.03 MDPE	0.10 MDPE	0.89 HDPE + 7% CaCO <sub>3</sub>	0.10 HDPE + 7% CaCO <sub>3</sub>	0.03 MDPE	2.93
	5	0.03 MDPE	0.10 HDPE + 7% CaCO <sub>3</sub>	0.89 HDPE + 7% CaCO <sub>3</sub>	0.10 HDPE + 7% CaCO <sub>3</sub>	0.03 MDPE	14.1
20	6	0.03 EP Copolymer	0.10 MDPE	0.89 HDPE + 7% CaCO <sub>3</sub>	0.10 MDPE	0.03 EP Copolymer	2.67- 4.12

The thickness of the HDPE and MDPE layers is expressed above in mils and does not take into account additional thickness resulting from cavitation. In addition, the WVTR is expressed above in g/100inch<sup>2</sup> · day.

Samples 1 and 3 were produced under similar conditions to establish a constant WVTR for comparison with WVTR values resulting from different physical conditions. Sample 2 was produced at a stretch temperature of 3°F lower than that of Sample 1. Comparing the WVTR of Samples 1 and 3 with that of Sample 2, it is readily apparent that a lower stretch temperature caused an increase in the WVTR of Sample 2.

Sample 4 was produced at conditions similar to Samples 1 and 3 except that layer 4 of Sample 4 was cavitated. The resulting increase in WVTR in Sample 4 compared to those of Samples 1 and 3 indicates that WVTR increases as a film is more cavitated.

The result in Sample 5 further supports the assertion drawn from the comparison of Sample 4 to Samples 1 and 3. In particular, tie layers 2 and 4 of Sample 5 were cavitated and the resulting WVTR was much higher than the WVTR of Samples 1 and 3. Clearly, increasing the cavitation of a film results in higher WVTR values.

Sample 6 shows a film structure wherein an ethylene-propylene copolymer is substituted for MDPE in the WVTR-controlling layers. This film has a higher WVTR in comparison to Samples 1 and 3 and it also has a high gloss of 61%.

**EXAMPLE 4**

TABLE III shows three layer film structures resulting from process conditions different than those used in obtaining the results of TABLE II. In particular, the results of TABLE III show that WVTR increases as cavitation increases regardless of what cavitant is used.

**TABLE III**

<u>Sample</u>	<u>Layer 1</u>	<u>Layer 2</u>	<u>Layer 3</u>	<u>WVTR</u>
7	0.17 MDPE	0.81 HDPE (M6211 Resin)	0.17 MDPE	0.2
8	0.17 MDPE	0.81 HDPE + 7% CaCO <sub>3</sub>	0.17 MDPE	4.0
9	0.17 MDPE	0.81 HDPE + 7% CaCO <sub>3</sub>	0.17 MDPE	7.2
10	0.17 MDPE	0.81 HDPE + 7% Epostar MA1002	0.17 MDPE	5.2

The thickness of the HDPE and MDPE layers is expressed above in mils and does not take into account additional thickness resulting from cavitation. In addition, the WVTR is expressed above in g/100inch<sup>2</sup> · day.

Sample 7 can be compared to Samples 8-10 to prove that cavitation increases the WVTR of a film. In particular, Sample 7 which is not cavitated had a resulting WVTR of 0.2 g/100inch<sup>2</sup> · day whereas Samples 8-10 which each had a cavitated core layer had resulting WVTRs of 4.0 g/100inch<sup>2</sup> · day, 7.2 g/100inch<sup>2</sup> · day and 5.2 g/100inch<sup>2</sup> · day, respectively.

Sample 10 is comparable to Samples 8 and 9 to illustrate that cavitating agents other than calcium carbonate (CaCO<sub>3</sub>) can be used to obtain similar results. In particular, Epostar MA 1002 was used as the cavitating agent in Sample 10. The resulting WVTR of 5.2 g/100inch<sup>2</sup> · day in Sample 10 supports the notion that cavitating agents other than calcium carbonate (CaCO<sub>3</sub>) can be used with the polyethylene films of the present invention.

**CLAIMS:**

1. A polyethylene film comprising:
  - (a) a base layer comprising polyethylene and a cavitating agent, said base layer  
5 having a first side and a second side; and
  - (b) at least one layer of a water vapor transmission rate (WVTR)-controlling  
material coextensive with one of said sides of said base layer;  
whereby said polyethylene film has a desired WVTR, wherein said base layer has a porous  
microstructure and a WVTR substantially higher than the desired WVTR for said polyethylene  
10 film.
2. A polyethylene film according to Claim 1, which further comprises at least one tie  
layer interposed between said base layer and said WVTR-controlling layer and coextensive  
with each of said base layer and said WVTR-controlling layer.  
15
3. A polyethylene film according to Claim 2, wherein said WVTR-controlling layer  
comprises an ethylene-propylene copolymer or an ethylene-propylene-butylene terpolymer,  
and each tie layer comprises a polyethylene comprising medium density polyethylene (MDPE)  
or a blend of high density polyethylene (HDPE) and low density polyethylene (LDPE).  
20
4. A polyethylene film according to Claim 1, which further comprises a second layer  
of WVTR-controlling material coextensive with the other side of said base layer.
5. A polyethylene film according to Claim 4, wherein:  
25 a first tie layer is interposed between said base layer and said first WVTR-  
controlling layer, coextensive with each of said base layer and said first WVTR-controlling  
layer, and  
a second tie layer is interposed between said base layer and said second WVTR-  
controlling layer, coextensive with each of said base layer and said second WVTR-controlling  
30 layer.

6. A polyethylene film according to Claim 1, wherein said WVTR-controlling material is a medium density polyethylene (MDPE) or a high density polyethylene (HDPE) having a density no greater than that of said polyethylene in said base layer.

5 7. A polyethylene film according to Claim 1, wherein said WVTR-controlling layer has a thickness of from 0.03 mil (3 gauge) to 0.15 mil (15 gauge).

8. A polyethylene film according to Claim 1, wherein said base layer has a thickness of from 0.5 mil (50 gauge) to 2.0 mil (200 gauge).

10

9. A method of producing a polyethylene film having a desired water vapor transmission rate (WVTR), comprising:

(a) adherently superimposing at least one layer of a WVTR-controlling material coextensively to a first side of a base layer having first and second sides; and

15

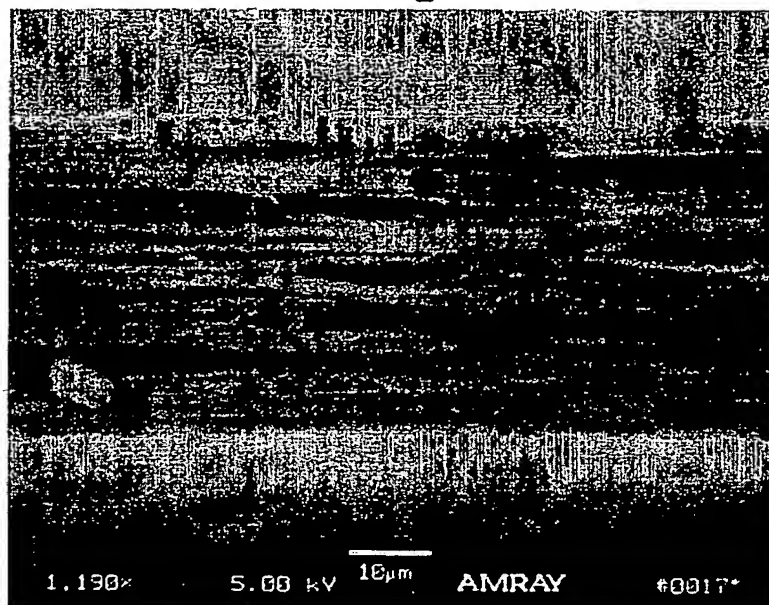
(b) biaxially orienting the composite polyethylene sheet resulting from step (a); whereby there is provided said polyethylene film having the desired WVTR, wherein said base layer has a porous microstructure and a WVTR substantially higher than the desired WVTR for said polyethylene film.

20

10. A method according to Claim 9, wherein step (a) comprises providing at least one tie layer interposed between said base layer and said WVTR-controlling layer and coextensive with each of said base layer and said WVTR-controlling layer.

1/2

5%  $\text{CaCO}_2$  in OPP

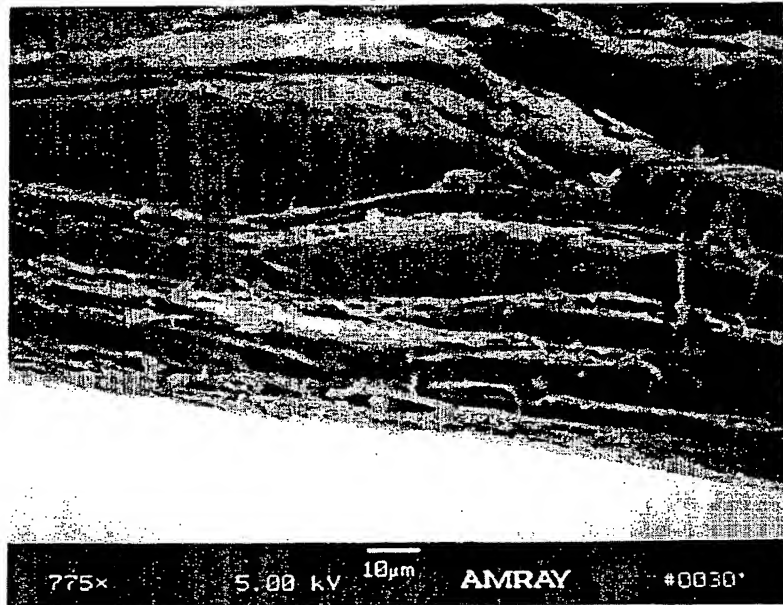


5%  $\text{CaCO}_3$  OPP FREEZE TD

*FIG. 1*

2/2

5%  $\text{CaCO}_3$  in BiHD



5%  $\text{CaCO}_3$  BiHD - FREEZE TD

*FIG. 2*



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/19788

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :B32B 5/28, 27/32

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/ 213, 317.9 319.7, 319.9, 515, 516 and 264/ 41, 290.2, 172.19, 172.19

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST: core same (polyethylene and void\$ and particle\$). (stretch\$ or orient\$).

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	US 5,885,721 A (SU et al.) 23 March 1999, see the entire document especially column 7, lines 54-64; column 8, line 61 to column 9, line 6; column 11, lines 60+; column 12, lines 36-51; column 14, lines 19-49; column 16, lines 64-67; and claims 1 and 6.	1-10
X	US 4,713,273 A (FREEDMAN) 15 December 1987, see the entire document especially figures 1 and 2; column 9, lines 65+; column 10, lines 1-58. See also column 3, lines 3+.	1-10
A	US 5,176,954 A (KELLER et al.) 5 January 1993, see the entire document especially example 8.	1-10

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 18 NOVEMBER 1999	Date of mailing of the international search report 23 DEC 1999
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer D. LAWRENCE TARAZANO <i>Regm Wilt</i> Telephone No. (703) 308-0651

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/19788

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

428/ 213, 317.9 319.7, 319.9, 515, 516 and 264/ 41, 290.2, 172.19, 172.19